

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C07C 59/06, 51/12, 51/235 C07C 51/43	A1	(11) International Publication Number: WO 92/05138 (43) International Publication Date: 2 April 1992 (02.04.92)
(21) International Application Number: PCT/US91/06626 (22) International Filing Date: 18 September 1991 (18.09.91) (30) Priority data: 585,629 20 September 1990 (20.09.90) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventor: DiCOSIMO, Robert ; 2817 Fawkes Drive, Wilmington, DE 19808 (US). (74) Agents: MORRISSEY, Bruce, W. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: MANUFACTURE OF HIGH-PURITY HYDROXYACETIC ACID (57) Abstract The invention relates to a process for the manufacture of high-purity, crystalline hydroxyacetic acid from crude hydroxyacetic acid made by the carbonylation reaction of formaldehyde and water in the presence of an organic acid and sulfuric acid by employing a crystallization step during the purification of the crude hydroxyacetic acid.		

LEDIGLICH ZUR INFORMATION

Code, die zur Identifizierung von PCT-Vertragsstaaten auf den Kopfbögen der Schriften, die internationale Anmeldungen gemäss dem PCT veröffentlichen.

AT	Österreich	ES	Spanien	ML	Mali
AU	Australien	FI	Finnland	MN	Mongolei
BB	Barbados	FR	Frankreich	MR	Mauritanien
BE	Belgien	GA	Gabon	MW	Malawi
BF	Burkina Faso	GB	Vereinigtes Königreich	NL	Niederlande
BG	Bulgarien	GN	Guinea	NO	Norwegen
BJ	Benin	GR	Griechenland	PL	Polen
BR	Brasilien	HU	Ungarn	RO	Rumänien
CA	Kanada	IT	Italien	SD	Sudan
CF	Zentrale Afrikanische Republik	JP	Japan	SE	Schweden
CG	Kongo	KP	Demokratische Volksrepublik Korea	SN	Senegal
CH	Schweiz	KR	Republik Korea	SU+	Sowjet Union
CI	Côte d'Ivoire	LI	Liechtenstein	TD	Tschad
CM	Kamerun	LK	Sri Lanka	TC	Togo
CS	Tschechoslowakei	LU	Luxemburg	US	Vereinigte Staaten von Amerika
DE	Deutschland	MC	Monaco		
DK	Dänemark	MG	Madagaskar		

+ Die Bestimmung der "SU" hat Wirkung in der Russischen Föderation. Es ist noch nicht bekannt, ob solche Bestimmungen in anderen Staaten der ehemaligen Sowjetunion Wirkung haben.

TITLEMANUFACTURE OF HIGH-PURITY HYDROXYACETIC ACID
FIELD OF THE INVENTION

5 The invention relates to a process for the manufacture of high-purity crystalline, hydroxyacetic acid from crude hydroxyacetic acid.

BACKGROUND OF THE INVENTION

10 Hydroxyacetic acid (HAA) is a useful commercial acid which is typically used for many industrial applications, such as metal cleaning, metal complexing and electroplating. For these applications a technical grade hydroxyacetic acid is sufficient. However, in applications where hydroxyacetic acid is used in
15 chemical synthesis, a purity of greater than 99% is highly desirable. An increased need for such high-purity HAA has been seen in recent years.

SUMMARY OF THE INVENTION

20 The present invention is an improvement in the existing and practiced process for the manufacture of HAA by the carbonylation of formaldehyde and water in HAA with a sulfuric acid catalyst, where a crystallization step is inserted into the purification process described in U.S. Patent 3,859,349 after the
25 anion exchange step, or after the stripper, or after the cation exchange step. With the insertion of the crystallization step, high-purity crystalline HAA is produced. By high-purity is meant a purity sufficient to be used in chemical synthesis. This usually means a
30 purity of 99% or greater.

 The crystallization step consists of cooling the solution of HAA in water to a temperature of from 10°C to -25°C, or more preferably to a temperature between 5°C and -18°C; and then, adding sufficient pure,
35 crystalline HAA to the cooled solution to seed the

solution and induce crystallization. The amount of pure HAA added can be as small as 0.01% by weight of the HAA present in the cooled or supercooled crude HAA solution.

The instant invention is an improvement over other methods because it affords HAA in greater than 99% purity, is simple to perform, is inexpensive to operate, does not require the use of hazardous organic solvents, is readily adaptable to large scale operations for use in a batch or continuous fashion and provides pure HAA as a dry solid which can be more conveniently used than aqueous solutions.

DESCRIPTION OF THE DRAWING

The drawing is a flow chart of the process of this invention.

DETAILED DESCRIPTION OF INVENTION

The process of this invention starts with the carbonylation of formaldehyde in water, in the presence of an organic acid, usually HAA, with sulfuric acid as a catalyst, and at pressures between 6,000 to 10,000 psig and temperatures of 210°C to 240°C. This carbonylation process is well known and is disclosed in U.S. Patents 2,153,064; 2,152,852 and 2,037,654. The disclosures of these patents are hereby incorporated by reference. This process produces a crude hydroxyacetic acid which must be purified prior to use or sale.

The crude hydroxyacetic acid made by the above carbonylation process will have the following typical composition in weight percent:

	hydroxyacetic acid	85%
30	formic acid	1.5
	sulfuric acid	1.5
	formaldehyde	1.5
	water	10.0
	methanol	0.5

The crude hydroxyacetic acid produced by this carbonylation process is purified by the process disclosed in U.S. Patent 3,859,349. In this process the crude hydroxyacetic acid is first contacted with
5 granulated activated carbon in a pulsed or fixed bed for color removal, the sulfuric acid present is then removed using a weak anion exchange column, low-boiling impurities (i.e., formaldehyde, formic acid, and methanol) are removed by heating at 110°C to 120°C, and
10 finally, a cation exchange resin is used to remove trace metals. Further description of this process can be found in U.S. Patent 3,859,349, which is hereby incorporated by reference.

The final product is a 70% technical-grade aqueous
15 solution; a typical analysis of this material is:

	total acid as HAA (wt. %)	71.3%
	free acid as HAA (wt. %)	62.4%
	formic acid (wt. %)	0.24%
	color (Gardner)	3
20	chloride (ppm)	2.6
	iron (ppm)	0.2

Hydroxyacetic acid is nonvolatile and cannot be distilled even under reduced pressure. Heating molten HAA readily produces polyhydroxyacetic acid
25 (polyglycolide) and water via a self-esterification reaction, thus distillation as a method of purification of HAA is not possible. Aqueous solutions of HAA are made up of mixtures of monomeric HAA and soluble polyacids (predominantly hydroxyacetic acid dimer) in
30 equilibrium, the ratio being determined by solution concentration. The polyacids can be hydrolyzed upon dilution of 70% HAA with water to 20% by weight or less, and refluxing or the addition of alkali to this diluted solution markedly increases the rate of this hydrolysis.
35 Although this dilution procedure can be used to convert

the HAA dimer to HAA monomer, a number of other impurities are also present in the 70% technical grade HAA; the components of a typical sample of 70% HAA are listed below:

5	HAA (wt. %)	62.4
	HAA dimer (wt. %)	8.8
	diglycolic acid (wt. %)	2.2
	methoxyacetic acid (wt. %)	2.2
	formic acid (wt. %)	0.24

10 The desired high-purity HAA is obtained by employing a crystallization procedure after the anion exchange step, after the stripper step, or preferably, after the cation exchange step.

In the crystallization procedure, the crude HAA
15 solution is cooled to a temperature of from 10°C (the reported melting point of 70% HAA) to -25°C (the temperature at which a supercooled solution of 70% HAA begins to solidify or freeze), or more preferably to a
20 temperature between 5°C and -18°C (the latter temperature being that at which the viscosity of the solution is observed to increase considerably). To the cooled solution is then added sufficient pure, crystalline HAA to seed the solution and induce
25 crystallization; the amount of pure HAA added can be as small as 0.01% by weight of the HAA present in the cooled or supercooled crude HAA solution.

Yields of high-purity HAA of from 6.6% to 24% are obtained by this method and the purity of the HAA obtained ranges from 99.3% to greater than 99.9%,
30 depending on the reaction conditions. Although it is known that solutions of HAA in water at relatively high concentration may supercool below the freezing point of the solution, it was unexpected that HAA of such high purity could be crystallized by the seeding of a cooled
35 or supercooled solution which contains such high levels

of undesirable impurities (i.e., diglycolic acid, methoxyacetic acid, formic acid, and glycolic acid dimer). In the absence of added pure, crystalline HAA to seed the cooled or supercooled solution,

- 5 crystallization of HAA may not readily occur; 70% technical grade HAA has been stored at 5°C for many weeks without crystallization of HAA.

The rate at which crystallization occurs, and the size of the resulting crystals, can be partially
10 controlled by selecting the appropriate temperature, and by either agitating or not agitating the seeded, cooled solution. Crystallization is slower and yields of crystalline HAA are lower at higher temperatures (i.e., 5°C as opposed to -18°C); however, the highest-purity
15 crystalline HAA is attained under these conditions. Agitation of the solution at a desired temperature will result in faster crystal formation, but the size of the crystals will be much smaller than those obtained without agitation. The crystal size is important when
20 considering filtration requirements; if the crystals are to be filtered and not washed to remove the mother liquor (which contains the undesirable impurities), a large crystal size will hold up less of this mother liquor. It is advantageous to produce pure HAA without
25 a wash to remove the mother liquor from the crystals. The highest purity crystalline HAA is obtained at higher temperatures (e.g., 5°C) and no stirring, although the yields are much less than those obtained at lower temperatures, with or without agitation. If it is
30 desirable to remove the mother liquor from the crystals by washing, cold water (2°C to 5°C), cold acetone (< 5°C), or ethyl ether can be used as a washing solvent, although other washing solvents may work equally as well. The process of this invention could be
35 used in a batch or continuous fashion.

The mother liquor recovered from the first crystallization can be recycled to the carbonylation reactor in the HAA manufacturing process, as a source of the required organic acid (see above), or a second crop of crystalline HAA may be obtained from this solution by first concentrating the mother liquor, then repeating the cooling and seeding procedure (an example of such a procedure appears below). Evaporation of the mother liquor may be performed at atmospheric pressure or under reduced pressure.

The process of the invention will now be described with reference to the figure.

Crude hydroxyacetic acid is made by the carbonylation process in reactor 1. The crude acid flows from through conduit 2 to absorber 3 which is packed with activated granular carbon. Decolorized crude acid 6 leaves the top of the absorber and is fed into the top of an anion exchange column 7 wherein the sulfuric acid present is removed. This column employs a weak anion exchange resin.

The effluent 10 from the anion exchanger 7 is fed into a stripper 11. Live steam 12 is sparged into the stripper and low boiling impurities are taken off overhead 13. The bottoms of the stripper are fed to a cation exchange column 15 wherein the resin removes trace metals.

The technical grade acid 16 from the cation exchanger is fed into a crystallizer 19 where the solution is cooled and, solid HAA of high purity is recovered.

Alternatively effluent 18 from the anion exchanger 7 or bottoms 17 from stripper 11 can be fed to a crystallizer 19. Mother liquor from the crystallizer can be recycled to the reactor 1 as illustrated by line 20.

EXAMPLESExample 1

Into a 15 mL polypropylene centrifuge tube was placed 4.0 mL of 70% HAA (3.89 g hydroxyacetic acid).
5 The tube and its contents were cooled to 5°C, then a few crystals of hydroxyacetic acid (Aldrich, 99% pure; < 2-3 mg) were added to the tube and the solution maintained at 5°C for 24 h. During this time a number of large (3-4 mm) hexagonal crystals were produced, and were
10 isolated by filtering the solution (no washing was performed) to yield 0.255 g (6.6% isolated yield) of hydroxyacetic acid. Analysis of this crystallized HAA by HPLC indicated it was greater than 99.9% pure hydroxyacetic acid; no formate, methoxyacetate, or
15 diglycolic acid were detected.

Example 2

Into a 100 mL Erlenmeyer flask was placed 50 mL of 70% HAA (43.2 g of hydroxyacetic acid), then the flask and its contents were cooled to -10 to -15°C in a dry
20 ice/acetone bath. To the resulting viscous solution was added hydroxyacetic acid (Aldrich, 99% pure; ca. 20 mg) and the solution was mixed by swirling the flask while maintaining the temperature at -10 to -15°C in the dry ice/acetone bath. Within a few minutes a fine white
25 precipitate was observed, and after ca. 15 minutes of mixing at -10 to -15°C, the cold solution was vacuum filtered, and the white solid allowed to air dry on the filter paper (it was not washed). The resulting white powder (10.2 g, 23.6% isolated yield) was analyzed by
30 HPLC: hydroxyacetic acid, 99.4%; diglycolic acid, 0.4%; methoxyacetic acid, 0.2%; dimer, 0%.

Example 3

Into a 1000-mL Erlenmeyer flask was placed 500 mL of 70% HAA (432 g of hydroxyacetic acid). The flask and
35 its contents were cooled to 5°C, then hydroxyacetic acid

(Aldrich, 99% pure; ca. 50 mg) was added and the solution allowed to stand at 5°C for 18 h. Large hexagonal crystals were observed to have formed, but most likely not in any greater yield than the 6.6% yield observed earlier at 5°C. The flask was cooled to -18°C over a period of 1 h, then the contents of the flask were mixed by vigorously swirling the flask intermittently over the next 5 h while maintaining the solution at -18°C. A fine, white crystalline solid was observed to precipitate during this time, and was collected by vacuum filtration and washed with ca. 100 mL of ethyl ether. The solid was dried under vacuum, then weighed (71.9 g, 16.7% yield), and subsequently analyzed by HPLC: hydroxyacetic acid, 99.3%; diglycolic acid, 0.6%; methoxyacetic acid, 0.1%; dimer, 0%.

Example 4

A 1-quart plastic bottle of 70% Hydroxyacetic acid (technical grade) from Belle (containing 1176 grams of solution) was placed in a freezer at -18°C for 4 hours, then 0.100 g of recrystallized HAA (99.3% pure) was added. The contents of the bottle were gently mixed to disperse the added HAA, then the bottle was stored in a freezer at -18°C for 63 h without agitation of the mixture. The resulting crystalline solid was collected by vacuum filtration of the mixture on a course-porosity glass fritted funnel, and the crystals allowed to air dry on the funnel (they were not washed). The crystals were then dried to a constant weight under vacuum at room temperature to yield 225 g of hydroxyacetic acid (27% isolated yield), which was analyzed by HPLC: hydroxyacetic acid, 99.9%; diglycolic acid, 0.1%; methoxyacetic acid, 0%; dimer, 0%.

A second crop of crystalline HAA was obtained from the remaining mother liquor (filtrate) from the first crystallization by first reducing the volume of this

filtrate from 785 mL to 690 mL by boiling down the solution. This solution was then cooled to -18°C for 4 h, then 0.10 g of recrystallized HAA was added to the solution and the mixture maintained at -18°C for an additional 22 h. The resulting crystals were collected by vacuum filtration (143 g, 17% isolated yield). Analysis of this second crop by HPLC gave the following results: HAA, 98.2%; HAA dimer, 1.2%; diglycolic acid, 0.3%; methoxyacetic acid, 0.3%. The HAA dimer was hydrolyzed to HAA by adjusting the pH of a solution of this 2nd crop to > 10 with conc. sodium hydroxide: HAA, 99.3%; HAA dimer, 0%; diglycolic acid, 0.3%; methoxyacetic acid, 0.4%.

Example 5

Into a 100 mL erlenmeyer flask was placed 50 mL of 70% HAA (43.2 g of hydroxyacetic acid), then the flask and its contents were cooled to -9°C . To the resulting viscous solution was added hydroxyacetic acid (Aldrich, 99% pure; ca. 20 mg) and the resulting mixture was maintained at -9°C without stirring or agitation. After 18 h the mixture was vacuum filtered using a fritted-glass funnel (the solid was not washed), and the crystalline solid dried under vacuum (1-2 mm Hg) to a constant weight at 26°C . The resulting white crystalline solid (5.54 g, 12.8% isolated yield) was analyzed by HPLC: hydroxyacetic acid, 99.7%; diglycolic acid, 0.3%; methoxyacetic acid, 0%; dimer, 0%.

The crystallization described above was repeated, except that the seeded solution was maintained at -9°C for 65 h before filtering. The resulting white crystalline solid (8.22 g, 19.0% isolated yield) was analyzed by HPLC: hydroxyacetic acid, 99.8%; diglycolic acid, 0.2%; methoxyacetic acid, 0%; dimer, 0%.

35

CLAIMS:

1. A process for the manufacture of high-purity,
5 crystalline hydroxyacetic acid (HAA) comprising:

- 10 (i) reacting formaldehyde and water in hydroxyacetic acid in the presence of sulfuric acid at pressures between 6,000 and 10,000 psig and temperatures of 210°C to 240°C to produce crude hydroxyacetic acid,
- (ii) decolorizing the crude hydroxyacetic acid by contact with a bed of granulated activated carbon,
- 15 (iii) removing sulfuric acid by contacting the product of step (ii) with a weak anion exchange resin,
- (iv) thereafter removing the remaining low-boiling impurities by live steam
20 stripping at temperatures of 110°C to 120°C,
- (v) removing metal impurities by contacting the product of step (iv) with a cation exchange resin to produce technical
25 grade hydroxyacetic acid,
- (vi) cooling the technical grade to a temperature from about 10°C to about -25°C,
- (vii) adding sufficient high-purity,
30 crystalline HAA to the cooled solution to induce crystallization, and
- (viii) recovering the crystalline HAA.

2. The process of Claim 1 wherein steps (vi),
35 (vii) and (viii) are conducted after step (iii).

3. The process of Claim 1 wherein steps (vi),
(vii) and (viii) are conducted after step (iv).

5 4. The process of Claim 1, 2 or 3 wherein the
crude HAA is cooled to about 5°C to about -18°C.

5. The process of Claim 1, 2 or 3 wherein the
crystalline HAA is recovered by filtration.

10

15

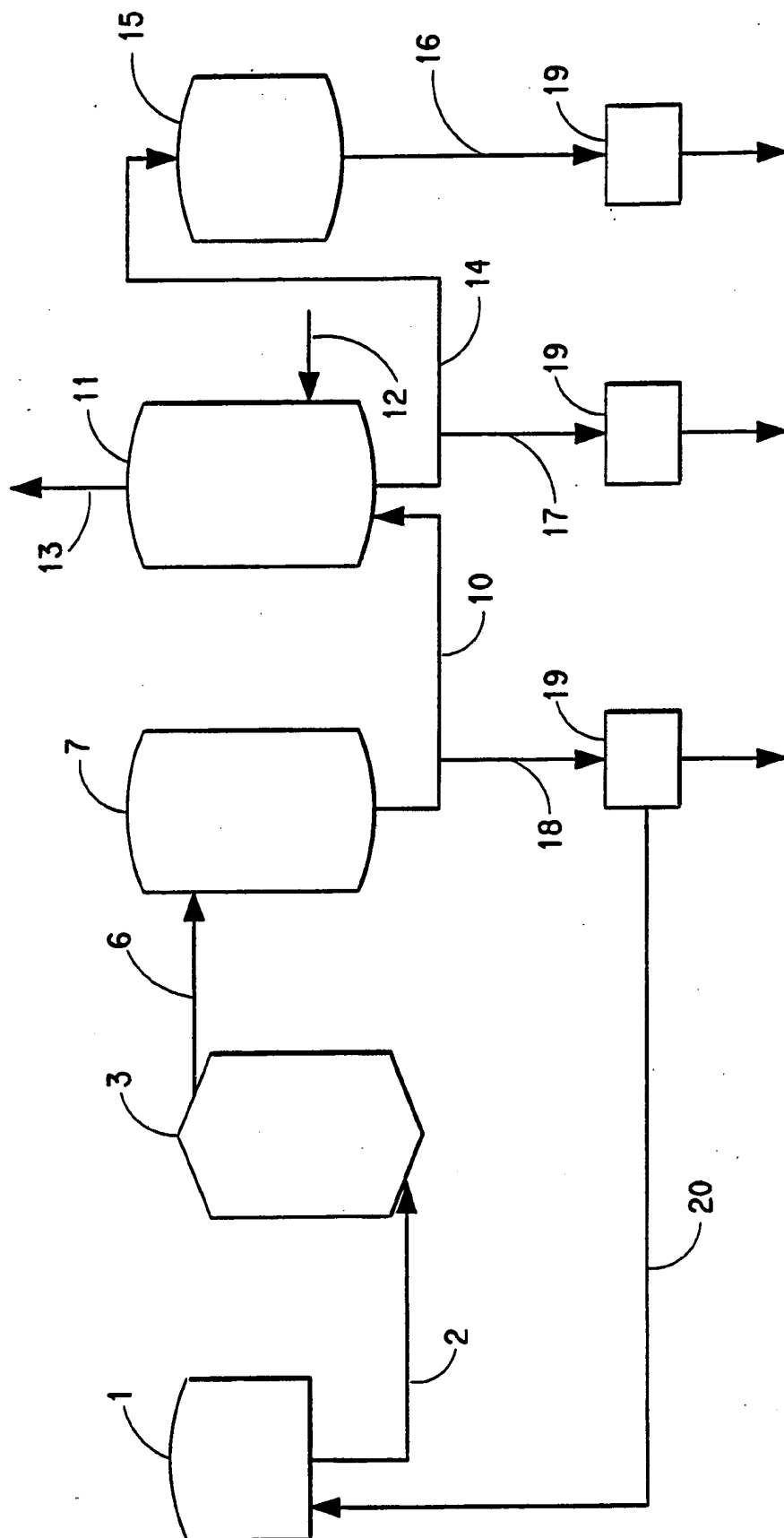
20

25

30

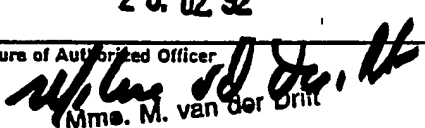
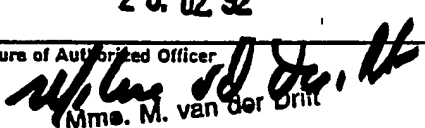
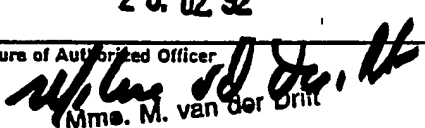
35

1/1



INTERNATIONAL SEARCH REPORT

International Application No PCT/US 91/06626

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 07 C 59/06, 51/12, 51/235, 51/43																	
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 30%; border-bottom: 1px solid black;">Classification System</td> <td style="border-bottom: 1px solid black;">Classification Symbols</td> </tr> <tr> <td style="height: 40px; vertical-align: bottom;">IPC5</td> <td style="vertical-align: bottom;">C 07 C</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched⁸</div>			Classification System	Classification Symbols	IPC5	C 07 C											
Classification System	Classification Symbols																
IPC5	C 07 C																
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category *</th> <th style="width: 70%; border-bottom: 1px solid black;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 20%; border-bottom: 1px solid black;">Relevant to Claim No.¹³</th> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 3859349 (N. F. CODY) 7 January 1975, see the whole document --</td> <td style="text-align: center; vertical-align: top;">1-5</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>Römpps Chemie-Lexikon, Acthe, neubearbeitete und erweiterte Auflage, pages 22444-2245, Otto-Albrecht Neumüller: "Kristallisation". --</td> <td style="text-align: center; vertical-align: top;">1-5</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>DE, C2, 2911944 (PPG INDUSTRIES, INC.) 4 October 1979, see the whole document --</td> <td style="text-align: center; vertical-align: top;">1-5</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>DE, A, 1643773 (AMERICAN CYANAMID CO.) 9 March 1972, see the whole document --</td> <td style="text-align: center; vertical-align: top;">1-5</td> </tr> </table>			Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	Y	US, A, 3859349 (N. F. CODY) 7 January 1975, see the whole document --	1-5	Y	Römpps Chemie-Lexikon, Acthe, neubearbeitete und erweiterte Auflage, pages 22444-2245, Otto-Albrecht Neumüller: "Kristallisation". --	1-5	A	DE, C2, 2911944 (PPG INDUSTRIES, INC.) 4 October 1979, see the whole document --	1-5	A	DE, A, 1643773 (AMERICAN CYANAMID CO.) 9 March 1972, see the whole document --	1-5
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³															
Y	US, A, 3859349 (N. F. CODY) 7 January 1975, see the whole document --	1-5															
Y	Römpps Chemie-Lexikon, Acthe, neubearbeitete und erweiterte Auflage, pages 22444-2245, Otto-Albrecht Neumüller: "Kristallisation". --	1-5															
A	DE, C2, 2911944 (PPG INDUSTRIES, INC.) 4 October 1979, see the whole document --	1-5															
A	DE, A, 1643773 (AMERICAN CYANAMID CO.) 9 March 1972, see the whole document --	1-5															
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>																	
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border-bottom: 1px solid black;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="text-align: center;">6th February 1992</td> <td style="text-align: center;">20.02.92</td> </tr> <tr> <td style="border-bottom: 1px solid black;">International Searching Authority</td> <td style="border-bottom: 1px solid black;">Signature of Authorized Officer</td> </tr> <tr> <td style="text-align: center;">EUROPEAN PATENT OFFICE</td> <td style="text-align: center;">  Mme. M. van der Drift </td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	6th February 1992	20.02.92	International Searching Authority	Signature of Authorized Officer	EUROPEAN PATENT OFFICE	 Mme. M. van der Drift							
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report																
6th February 1992	20.02.92																
International Searching Authority	Signature of Authorized Officer																
EUROPEAN PATENT OFFICE	 Mme. M. van der Drift																

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	US, A, 2153064 (ALFRED T. LARSON) 4 April 1939, see the whole document --	1
A	US, A, 2152852 (DONALD JOHN LODER) 4 April 1939, see the whole document --	1
A	US, A, 2037654 (ALFRED T. LARSON) 14 April 1936, see the whole document -- -----	1

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. PCT/US 91/06626**

SA 52956

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 31/10/91. The European Patent office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3859349	07/01/75	BE-A- 810280	29/07/74
		FR-A-B- 2217307	06/09/74
		GB-A- 1429591	24/03/76
		JP-A- 49124025	27/11/74
		NL-A- 7401188	19/08/74
DE-C2- 2911944	04/10/79	GB-A-B- 2017697	10/10/79
		JP-C- 1169923	17/10/83
		JP-A- 54130519	09/10/79
		JP-B- 57057451	04/12/82
		US-A- 4140866	20/02/79
DE-A- 1643773	09/03/72	CH-A- 493515	15/07/70
		GB-A- 1194501	10/06/70
US-A- 2153064	04/04/39	NONE	
US-A- 2152852	04/04/39	NONE	
US-A- 2037654	14/04/36	NONE	

For more details about this annex : see Official Journal of the European patent Office, No. 12/82

EPO FORM P0479